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Applicant(s): CIBA GEIGY AG ;

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 REBER



(54) SPECTRAL SENSITISING DYES

(71) We, CIBA-GEIGY AG, a Swiss body corporate, of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel spectral sensitising dyes for photographic materials. This invention is divided out of our co-pending application no. 11187/75 (Serial No. 1529201) which was filed on 20 February 1976.

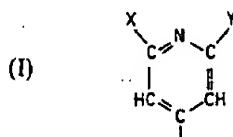
According to the present invention there is provided a spectral sensitising dinuclear-cyanine dye or merocyanine dye which has attached either to a heterocyclic nucleus of the dye or to the methine chain of the dye an azine group which comprises at least one leaving group and which is reactive with a hydrophilic colloid which contains an SH—, NH₂—, NH—, OH—, —CONL₁L₂ group, where L₁ and L₂ are each hydrogen atoms or lower alkyl groups or a —COOH group. By lower alkyl or alkoxy group is meant an alkyl or alkoxy group having from 1 to 5 carbon atoms.

Examples of hydrophilic colloids which contain SH—, NH₂—, NH—, —OH, —CONL₁L₂ or —COOH groups hereinafter referred to as reactable groups are polypeptides, skin tissues, agar-agar, polyvinyl alcohol, casein, albumen, cellulose derivatives such as phthalated cellulose, carboxy methyl cellulose and methyl cellulose as well as hydrophilic homo- or copolymers of acrylic or methacrylic acid and polyvinyl-pyrrolidone having reactable substituent groups.

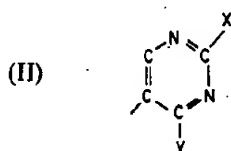
By the phrase "an azine group which is reactive with a hydrophilic colloid which contains a reactable group as hereinbefore defined" which is used hereinafter there is meant an azine group which contains at least one leaving group which is able to react with an SH—, NH₂—, NH—, —OH, —CONL₁L₂ or —COOH group in a hydrophilic altered to form a chemical bond with the loss of the or at least one leaving group. The term "azine" means a pyridine, diazine or triazine group.

The most useful leaving groups present on the azine nucleus are chlorine, bromine and ammonium or substituted ammonium such as N-methyl-morpholinium.

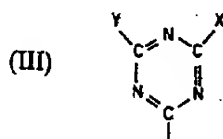
Examples of such reactive groups are azines of the general formula



diazines of the general formula



and triazines of the general formula



wherein in the above three formulae at least one of X and Y is a leaving group and the other if not a leaving group is a hydroxy or lower alkoxy group.

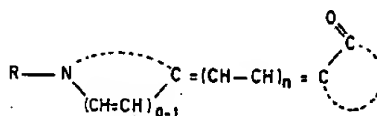
By dinuclear cyanine and merocyanine spectral sensitizers for light sensitive heavy metal compounds are meant dinuclear cyanine and merocyanine dyestuffs which when in contact with a light-sensitive heavy metal compound are able to alter the spectral sensitivity of the light-sensitive heavy metal compound by altering the spectral absorption curve of the metal compound for example by increasing its light sensitivity to light of a particular wave band and/or by rendering the heavy metal compound sensitive to light of a particular wave band to which it was not initially light sensitive. For example silver halides are sensitive only to blue light but spectral sensitizing dyes can be brought into contact with silver halide to render it light sensitive not only to blue light but to green and red light and sensitive to light far into the infra-red region of the spectrum.

Examples of light-sensitive heavy metal compounds are silver halides such as silver chloride, silver bromide and silver iodide and mixtures thereof for example silver iodobromide, lead halide, zinc oxide, zinc sulphide, cadmium sulphide and titanium dioxide.

Each of the metal compounds has its preferred classes of dinuclear cyanine and/or merocyanine spectral sensitizers and such dyes which spectrally sensitise others of these metal compounds will not spectrally sensitise others of these metal compounds. However the term spectral sensitizers can also be used to cover the spectral sensitization of reversal light-sensitive systems such as direct positive silver halide emulsions in which case the spectral sensitiser when in contact with the silver halide crystals alters their spectral absorption but in fact it can be said to act as a desensitizer in that instead of increasing the photographic speed of the silver halide by passing electrons to the silver halide, it decreases the photographic speed of the silver halide by acting as an electron acceptor.

The term dinuclear cyanine dye used herein is defined in Hamer in "The Cyanine Dyes and Related Compounds" which was published in 1964 by Interscience as one of the Monographs relating to The Chemistry of Heterocyclic Compounds. On page 25 of this book a dinuclear cyanine is defined as a mono-acid salt in which the nitrogen atoms of the two heterocyclic nuclei are linked by a chain of conjugated double bonds so that this chain necessarily consists of an odd number of carbon atoms. The nitrogen atom of one nucleus is tertiary and the other is quaternary. However in this application the term dinuclear cyanine dye includes also azacyanine dyes and diazacyanine dyes, that is to say dyes having two heterocyclic nuclei linked by a chain of conjugated double bonds but wherein in the conjugated chain either one or two of the carbon atoms have been replaced by a nitrogen atom. The term di-nuclear cyanines also uses certain tri-nuclear and polynuclear cyanine dyes referred to in the Hamer book Chapter XV.

The term merocyanine dye as used herein is defined by Hamer in "The Cyanine Dyes and Related Compounds" as non-ionic compounds of the structure

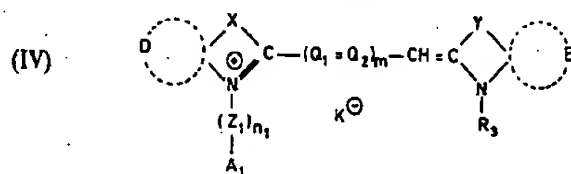


wherein n is 0—3.

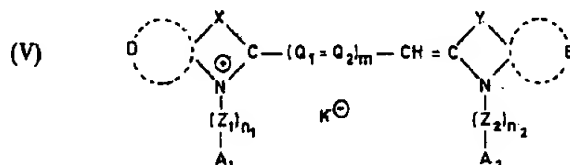
Thus the methine chain which links the two nuclei is either a direct link or even numbered.

The novel spectral sensitizers of the present invention are of use as sensitizers for normal negative working silver halide emulsions and in particular for gelatino silver halide emulsions which on exposure and development yield a negative image.

According to a preferred embodiment of the invention there is provided a spectral sensitizing dinuclear cyanine dye of the general formula



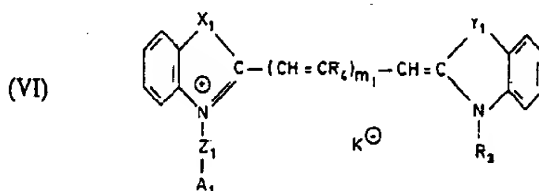
or the general formula



wherein the above two terms X and Y are each $-\text{C}(\text{R}_1\text{R}_2)-$ where R_1 and R_2 are each hydrogen atoms or lower alkyl groups, $-\text{CH}=\text{CH}-$, $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$ or $-\text{NR}_3-$, where R_3 is a lower alkyl group, D and E each represent the atoms necessary to complete a benzene or naphthalene ring system which may be optionally substituted, m is 0, 1 or 2, Z_1 and Z_2 are each a linking group, each of n_1 and n_2 are 0 or 1, R_2 is a lower alkyl, lower alkoxy, carboxy lower alkyl or sulphonyl lower alkyl group, K is an anion, and A_1 and A_2 are each an azine group which is reactive with a hydrophilic colloid which contains a reactable group as hereinbefore defined and $-(\text{Q}_1=\text{Q}_2)-$ represents a conjugated double bond system.

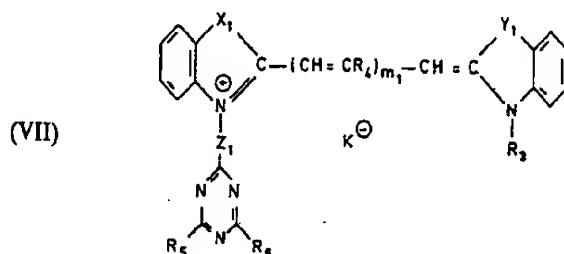
Preferably in the above two formulae $-(\text{Q}_1=\text{Q}_2)-$ is a conjugated carbon to carbon double bond system wherein optionally one at least of the carbon may be substituted by lower alkyl group. However, when m is 1 $-(\text{Q}_1=\text{Q}_2)-$ may represent the linkage $-\text{N}=\text{CH}-$ or $-\text{N}=\text{N}-$ that is to say the dyes may be azacyanines or diazacyanines. Preferably in both of the formulae (IV) and (V) m is 1 and $-(\text{Q}_1=\text{Q}_2)-$ represents the linkage $-\text{CH}=\text{CR}_4-$ wherein R_4 is a hydrogen atom or an ethyl, a methyl or a phenyl group, that is to say the dyes are dinuclear trimethincyanine dyes.

One class of dyes of formula IV are dyes of the following formula



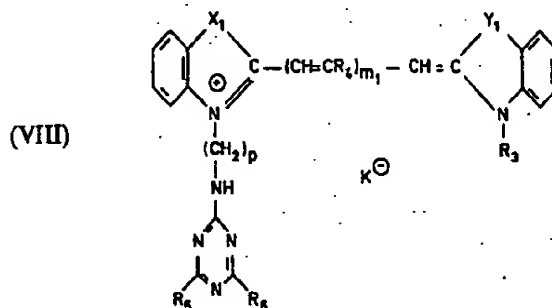
wherein X_1 and Y_1 are each $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$ or $-\text{NR}_3-$, m_1 is 0 or 1, R_3 , R_4 , R_5 , Z_1 , A_1 and K have the meanings assigned to them above.

Particularly useful dyes of this type have the general formula



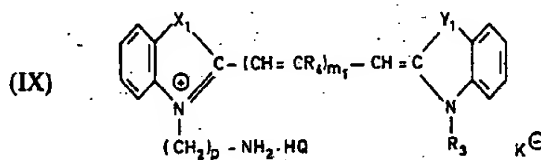
where at least one of R_5 and R_6 is a leaving group and the other if not such a group is a hydroxy or lower alkoxy group, and X_1 , Y_1 , R_3 , R_4 , Z_1 , m_1 and K have the meanings assigned to them above:

A particularly useful linking group Z_1 in dyes of formula (VII) is provided by the group $-(CH_2)_p-NH-$ where p is 2-5. Dyes of this type have the general formula

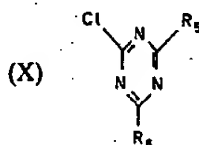


5 wherein X_1 , Y_1 , R_3 , R_4 , R_5 , R_6 , m_1 , p and K^+ have the meanings assigned to them above.

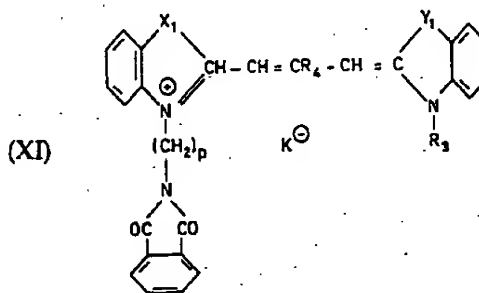
Dyes of formula (VIII) may be prepared by reacting a methinecyanine dye of formula



10 wherein X_1 , Y_1 , R_3 , R_4 , p , m_1 and K have the meanings assigned to them above and Q is I, Cl or Br with a triazine of the general formula

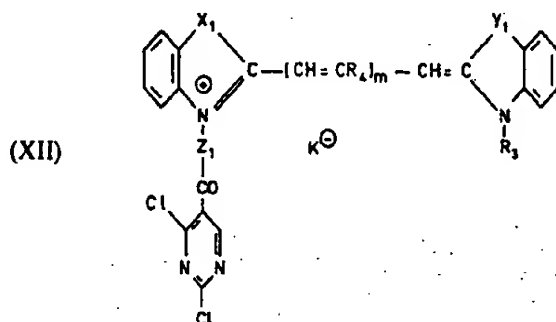


wherein R_5 and R_6 have the meanings assigned to them above. Dyes of formula (IX) may be prepared from dyes of the general formula (XI)



by hydrolysing the dye with a hydrohalo acid. (e.g. hydrochloric acid).

Another class of dyes of formula VI of particular interest are dyes of the general formula

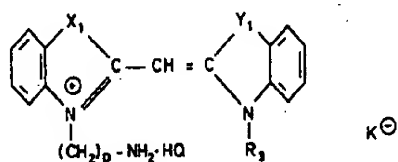


wherein X_1 , Y_1 , R_3 , R_4 , K , m , and Z_1 have the meanings assigned to them above.

Especially preferred dyes of formula (XII) are those wherein both X_1 and Y_1 are $-S-$ and Z_1 is a linking group $(CH_2)_p-NH-$ where p is 2-5 and m is 0.

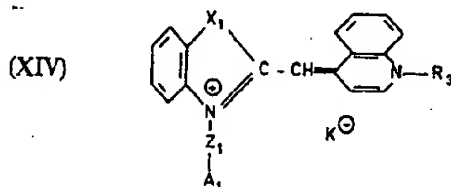
The preferred trimethincyanine dyes of formula XII may be prepared by reacting a trimethincyanine dye of formula IX with 2,4-dichloropyrimidine-5-carboxylic acid chloride.

Monomethincyanine dyes of formula XII may be prepared by reacting a monomethincyanine dye of formula XIII

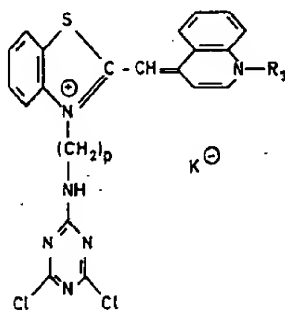


wherein X_1 , Y_1 , p , R_3 and K have the meanings assigned to them above and Q is I, Cl or Br with 2,4-dichloropyrimidine-5-carboxylic acid chloride. This preparation is described in Example 6.

Another class of monomethincyanine dyes of particular interest are dyes of the general formula

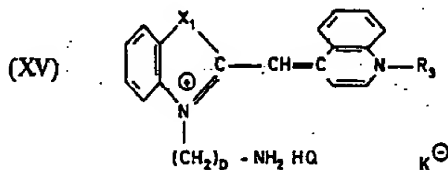


wherein A_1 , X_1 , R_3 , K and Z_1 have the meanings assigned to them above, for example the dye of the formula



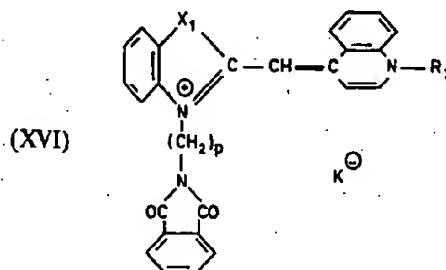
wherein R_3 and K have the meanings assigned to them above.

Dyes of this latter type of formula (XIV) may be prepared by reacting a monomethincyanine dye of the formula



wherein X_1 , p , R_3 , Q and K have the meanings assigned to them above with a compound $A_1\text{—Cl}$ where A_1 has the meaning assigned to it above. This preparation is described in Example 5 under (4.12).

The dyes of the above formula XV may be prepared from a dye of the general formula



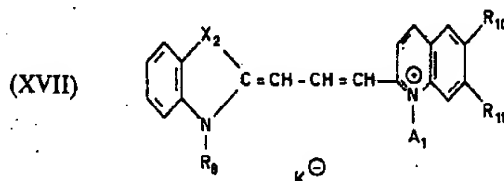
wherein X_1 , p , R_3 and K have the meanings assigned to them above.

The above preparation works particularly well when p is 3 and hydrobromic acid is used.

An example of a dye of formula (VIII) and a process for preparing this dye are set forth in Example 4 which follows.

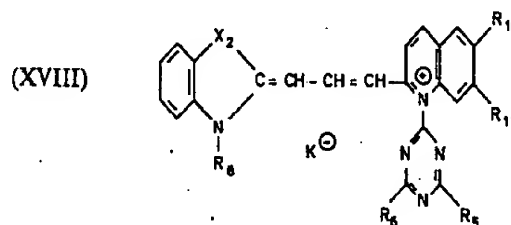
Another class of dyes of formula (IV) or of formula (V) are dyes wherein at least one of n_1 and n_2 is 0. That is to say dyes wherein the reactive group A_1 is linked directly to the ring nitrogen of the heterocyclic group.

One specific class of dyes of this type are dyes of the following general formula



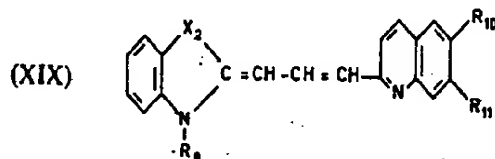
wherein X_2 is —O— , —S— , —Se— , —NH— or $\text{—C(R}_1\text{R}_2\text{)—}$, R_{10} and R_{11} are each hydrogen atoms or lower alkyl or lower alkoxy groups. R_8 is lower alkyl, lower alkoxy, carboxy-lower alkyl or sulphy-lower alkyl and A_1 and K^+ have the meanings assigned to them above.

A particularly useful dye is obtained when A_1 is a triazine nucleus having two leaving groups. Dyes of this type have the general formula



wherein X_2 , R_8 , R_{10} , R_{11} , K^+ , R_5 and R_6 have the meanings assigned to them above.

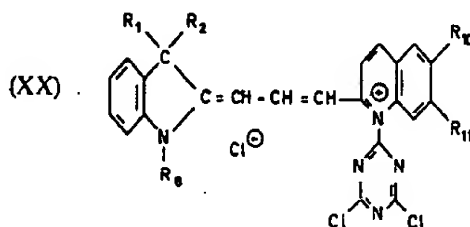
Dyes of general formula (XVIII) may be prepared by reacting a cyanine base of the general formula



wherein X_2 , R_8 , R_{10} and R_{11} have the meanings assigned to them above with a triazine of the general formula (X).

The reaction works particularly well and an especially useful dye is obtained when the triazine of formula (X) is cyanuric chloride.

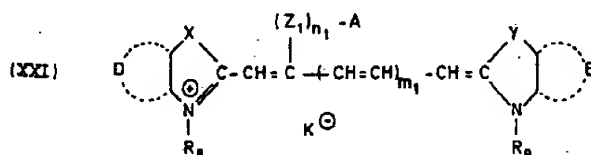
A very interesting class of dyes of this type are obtained when X_2 in formula (XVIII) is $-C(R_1R_2)-$. Dyes of this type have the general formula



wherein R_1 , R_2 , R_8 , R_{10} and R_{11} have the meanings assigned to them above.

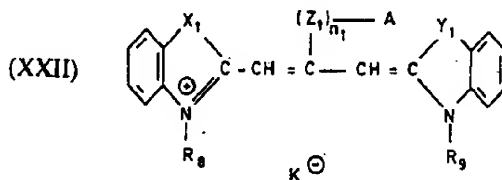
The preparation of a dye of formula (XX) is set forth hereinafter in Example 7.

According to another embodiment of the invention there is provided a spectral sensitising carbocyanine dye of the general formula



wherein X and Y are each $-C(R_1R_2)-$ wherein R_1 and R_2 are each a hydrogen or lower alkyl, $-\text{CH}=\text{CH}-$, $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$ or $-\text{NR}_7-$, D and E each represent the atoms necessary to complete a benzene or naphthalene ring system which may be optionally substituted m_1 is 0 or 1, R_8 and R_9 are each lower alkyl, lower alkoxy alkyl, carboxy lower alkyl or sulfo-lower alkyl groups, Z_1 is a linking group, n_1 is 0 or 1. K is an anion, A is an azine group which is reactive with a hydrophilic colloid which contains a reactable group as hereinbefore defined.

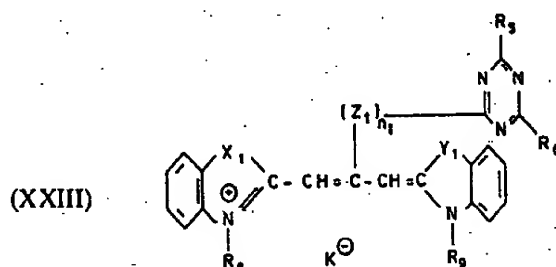
Preferred dyes of formula (XXI) are dyes of the general formula



wherein X_1 and Y_1 are each $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$ or $-\text{NR}_7-$ and K , Z_1 , n_1 , A , R_8 , R_9 and R_7 have the meanings assigned to them above.

Particularly useful dyes are obtained when A is a triazine nucleus having two leaving groups.

Dyes of this type have the general formula

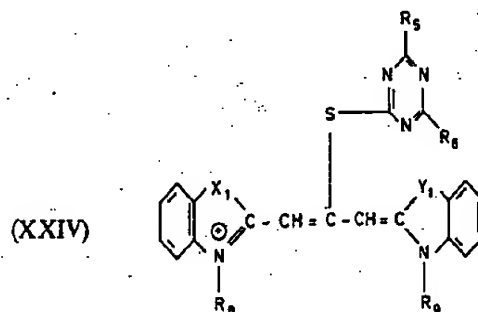


wherein X_1 , Y_1 , Z_1 , n_1 , R_5 , R_6 , R_8 , R_9 and K have the meanings assigned to them above.

5

In one particular embodiment Z_1 is S and n_1 is 1.
Dyes of this type have the following general formula

5

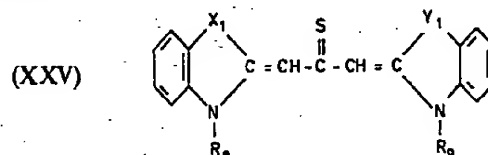


wherein X_1 , Y_1 , R_5 , R_6 , R_8 , R_9 and K have the meanings assigned to them above.

Dyes of formula (XXIV) may be prepared by reacting a compound of the general formula

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wherein X_1 , Y_1 , R_8 and R_9 have the meanings assigned to them above with a triazine of general formula (X) as hereinbefore set forth.

The reaction proceeds particularly well and an especially useful dye is obtained when the triazine of formula (X) is cyanuric chloride and in such case in the resulting dye of formula (XXIV) both R_5 and R_6 are chlorine atoms. An example of a dye of formula (XXIV) and a process for the production of such dyes are given in Example 3 hereinafter set forth.

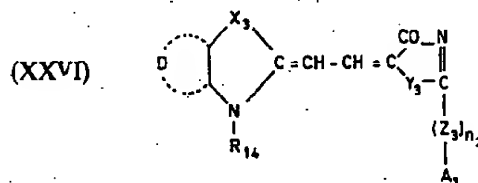
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According to another embodiment of the present invention there is provided a spectral sensitising merocyanine dye of the general formula

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wherein X_3 is $-C(R_1R_2)-$ wherein R_1 and R_2 are each a hydrogen atom or a lower alkyl group. $-CH=CH-$, $-O-$, $-S-$, $-Se-$ or $-NR_7-$ wherein Y_3 is $-O-$, $-S-$, $-Se-$ or $-NR_7-$, D represents the atoms necessary to complete a benzene or naphthalene ring system which is optionally substituted, R_{14} is lower

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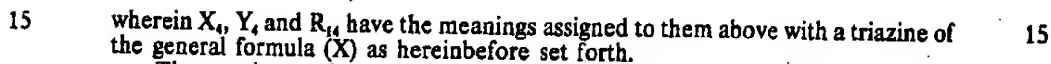
Preferred dyes of formula (XXVI) are dyes of formula



A particularly useful class of dyes of formula (XXVII) are dyes wherein A_1 is a triazine nucleus having two leaving groups. Such dyes have the general formula



Dyes of formula (XXVIII) may be prepared by reacting a merocyanine dye of general formula



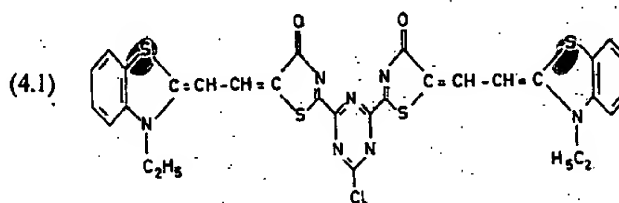
However, in such case as cyanuric chloride is particularly reactive a bis-merocyanine dye of the following general formula



25 The preparation of a merocyanine dye of this type is described in Example 1, which follows.

25

200 g of a 5% strength gelatine solution are warmed to 45°C and adjusted to a pH of 8.5 by the addition of dilute sodium hydroxide solution. 73.8 mg (0.1 millimol) of the sensitising dyestuff of the formula



dissolved in 100 ml of trifluoroethanol, are added to this solution over the course of 2 minutes, whilst stirring. After stirring for two hours at 45°C, the temperature is gradually raised to 60°C and the trifluoroethanol is removed under moderately reduced pressure (about 20 millibars). By adding water, the weight is made up to 200 g and the pH is then adjusted to 4.9 by the addition of molar nitric acid. A completely clear solution is obtained.

In order to prove that the dyestuff has completely reacted with the gelatine and does not diffuse out in an aqueous medium, a sample of the solution is made to flocculate by means of a saturated sodium sulphate solution. After decanting the supernatant colourless solution from the flocculate, the latter is again taken up in water and dialysed through a cellulose acetate membrane until the sulphate ions have disappeared. The bond between the gelatine and the dyestuff can also be proved electrophoretically.

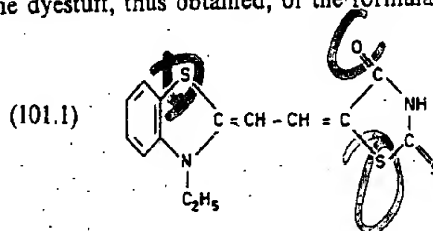
A light-sensitive silver halid emulsion is prepared as follows from the solution containing 5% of gelatine and the sensitising dyestuff bonded to the gelatine: 3 ml of a 1 molar ammonia solution are added to 150 g of the gelatine-dyestuff solution containing 55.35 mg of the bonded dyestuff. 150 ml of a 4 molar silver nitrate solution and 150 ml of a solution containing, per litre, 4 mols of ammonium bromide and 3.2 ml of 25% strength aqueous ammonia are simultaneously added over the course of 70 minutes. Even feed of the two solutions is controlled in such a way that a pAg of 7.0 is maintained during the period of precipitation.

For the purpose of removing the ammonium nitrate formed by the reaction, the emulsion is then flocculated in the usual way, decanted and washed and then again redispersed in ordinary gelatine solution. A customary sulphur-gold ripening is then carried out at 54°C for 50 minutes. Finally, the completely ripened emulsion is coated onto a polyester base, to give a layer thickness corresponding to 3.5 g of silver per m², and dried. It is of course necessary to exclude photographically active light during the preparation of the emulsion and the coating and drying. A wedge spectrogram of this material shows a sensitisation between 480 and 650 nm with a maximum at 580 nm. The content of sensitiser, calculated as sensitising dyestuff, is 0.1 millimol per mol of silver bromide; 1/5th of the sensitiser is lost during the flocculation and subsequent washing.

The dyestuff of the formula (4.1) was be prepared as follows:

22 g of 2-acetanilidovinyl-3-ethylbenzthiazolium iodide and 6.3 g of rhodanine are warmed in 500 ml of methanol under a reflux condenser until a clear solution is formed. 8 ml of triethylamine are slowly added to the boiling solution, and reflux is maintained for a further 2 hours. After cooling for one hour, the dyestuff is separated off, washed with 500 ml of ethanol and 200 ml of chloroform, boiled up with 260 ml of a (10:3) mixture of ethanol and chloroform, filtered off and dried at 60°C for 24 hours.

1.6 g of the dyestuff, thus obtained, of the formula

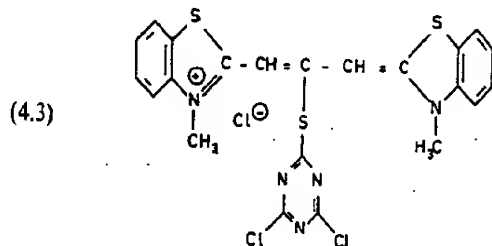


are dissolved in 100 ml of boiling dioxane and carefully added to 300 ml of tetrahydrofuran. After cooling to room temperature, 1 g of cyanuric chloride is added and then 0.7 ml of collidine in 10 ml of tetrahydrofuran is added dropwise over the course of half an hour, whilst stirring. The addition of 1 g of cyanuric chloride and of 0.7 ml of collidine in 10 ml of tetrahydrofuran is repeated. 0.9 ml of triethylamine in 10 ml of tetrahydrofuran is then added and

the mixture is stirred for half an hour and poured into 1 litre of acetone. 0.9 ml of triethylamine is added, the mixture is stirred for a quarter of an hour and then 0.9 ml of triethylamine is added once more, the colour of the solution becoming reddish. After leaving to cool overnight to 5°C, about 0.1 g of solid is obtained by filtration, washing with acetone and drying. The dry residue obtained from the filtrate by evaporation under reduced pressure is treated with a (1:1) mixture of acetone and ether, filtered off, washed with ether and then with acetone and dried. About 1 g of crude product is obtained and this is triturated with 50 ml of water, filtered off and thoroughly washed with water, then with acetone and finally with ether. After drying in vacuo at 80°C, about 0.25 g of dyestuff of the formula (4.1) remains, which shows an absorption maximum of 525 nm in methanol.

Example 2.

154.8 mg = 0.28 millimol of the dyestuff of the formula



dissolved in 70 ml of trifluoroethanol, are added to 300 g of a 5% strength gelatine solution. The solution is treated as indicated in Example 1. After removing the solvent, likewise as indicated in Example 1, a silver bromide emulsion is prepared as follows from the 5% strength gelatine solution containing the dyestuff:

4 ml of a 1 molar ammonia solution are added, at a temperature of 55°C, to 206 g of the dyestuff-containing gelatine solution which contains 106.3 mg of the bonded dyestuff (4.3). All the following operations are carried out in the dark:

300 ml each of 4 molar silver nitrate solution and 4 molar ammonium bromide solution, 3.2 ml of 25% strength aqueous ammonia solution having been added per litre of the latter, are added simultaneously over the course of 110 minutes.

The feed rates are adjusted to one another in such a way that a constant pAg of 6.5 is maintained.

After the customary flocculation, decanting and washing, the flocculate is redispersed in ordinary gelatine and the resulting emulsion which contains cubic silver bromide crystals, is divided into three equal parts, each of which contains 0.3 mol of silver bromide.

A separate chemical ripening is carried out for each of these three parts, C, D and E, under the conditions described in Example 1. A solution of 60 mg of the dyestuff (4.2) in 120 ml of methanol is added to part C before ripening. Part D is provided with an addition of 15 mg of the dyestuff (4.2) dissolved in 120 ml of methanol. The addition to part E consists of only 120 ml of methanol (control experiment).

Accordingly, the emulsion C contains, per mol of silver bromide, 0.16 millimol of the dyestuff (4.3) as well as 0.364 millimol of the dyestuff (4.2), in a form which can be adsorbed on the surface of the silver bromide grains. The emulsion D contains, per mol, the same amount of dyestuff (4.3) bonded to gelatine and in addition 0.091 millimol of the dyestuff (4.2) adsorbed on the grain surface.

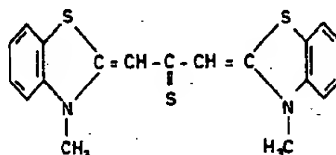
Table 2 shows that a good sensitisation is already obtained for the case of emulsion E, whilst in the case of emulsion D a further increase of the sensitivity can be observed due to the additionally adsorbed dyestuff (4.2).

A marked desensitisation, however, caused by the excessive amount of adsorbed dyestuff (4.2), is demonstrated for emulsion C.

TABLE 2

1. Emulsion	Log E			5. Log E (-blue) -Log E (blue)	Sensitiser, mmols/mol of AgBr	
	2. white	3. blue	4. -blue		6. Dyestuff (4.3) bonded	7. Dyestuff (4.2)
C	-0.48	0.80	-0.36	-1.16	0.16	0.364
D	-0.92	0.26	-0.82	-1.08	0.16	0.091
E	-0.26	0.36	0.10	-0.26	0.16	—

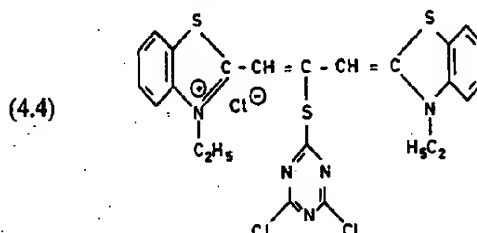
The dyestuff of the formula (4.3) can be manufactured by condensing the compound of the formula



5 with cyanuric chloride in anhydrous chloroform, as indicated in Example 1. 5

Example 3.

116.2 mg (0.2 millimol) of the dyestuff of the formula



10 dissolved in 70 ml of trifluoroethanol, are reacted with 200 g of a 5% strength
gelatine solution in the same manner as described in Example 1. After removal of
the solvent, the gelatine solution containing the dyestuff is made up again to 200 g,
corresponding to the original gelatine content of 5%. A sample of 190 g,
corresponding to 110 mg of bonded dyestuff (4.4) is taken from this solution. A
silver bromide emulsion with cubic crystals is prepared from this sample by the
15 procedure described in Example 4, but using 250 ml each of 4 molar silver nitrate
solution and of 4 molar ammonium bromide solution containing ammonia. After
the customary purification by flocculation, decanting and washing, a sulphur-gold
ripening is carried out at 54°C for 50 minutes.

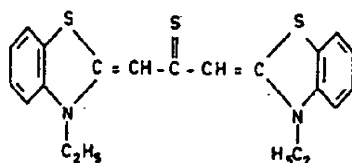
20 The emulsion is then coated onto a polyester base to give a layer thickness
corresponding to 3 g of silver per m², and is dried.

The sensitometric data of this emulsion which contains, per mol of silver
bromide, 0.19 millimol of the dyestuff (4.4) is represented in Table 4. It shows a
strong sensitisation between 480 and 690 nm.

TABLE 4

1. Emulsion	Log E			5. Log E (-blue) -Log E (blue)	Sensitiser, mmol/mol of AgBr	
	2. white	3. blue	4. -blue		6. In gelatine (4.4)	7. Adsorbed
K	-0.58	0.50	-0.50	-1.0	0.19	—

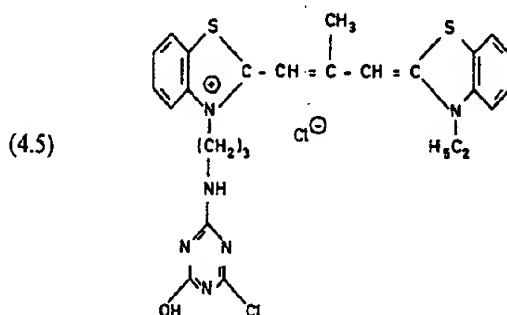
The dyestuff of the formula (4.4) can be prepared as follows:
1.62 g of the dyestuff of the formula



are extracted in a Soxhlet apparatus with 800 ml of dry acetone, until the liquid runs down colourless. 3 g of cyanuric chloride dissolved in 100 ml of acetone are added to the solution cooled to room temperature, whilst stirring. After about 2 hours of further stirring at room temperature, the dyestuff of the formula (4.4) crystallises out. It is filtered off and washed with acetone and then with ether. λ_{\max} in chloroform at 570 and 610 nm.

Example 4.

229.3 mg (0.4 millimol) of the dyestuff of the formula

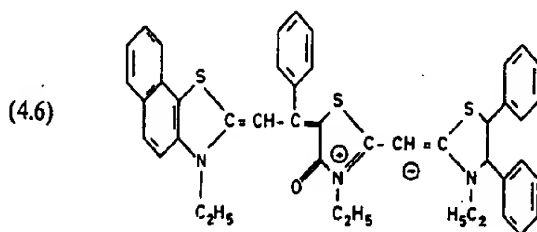


dissolved in 160 ml of methanol, are reacted with 200 g of a 5% strength gelatine solution according to the procedure described in Example 1. After removal of the solvent, the solution is made up again to 200 g with water. A sample of 190 g is taken and a silver bromide emulsion with cubic crystals is prepared therefrom as described in Example 4. After the customary purification by flocculation, decanting and washing, three equal samples, S, T and U, each containing 0.15 mol of silver bromide, are taken. The three samples separately are allowed to ripen chemically, as described in the example, each with the following additions:

Part S: 36 ml of methanol

Part T: 4.4 mg of the dyestuff (4.6), dissolved in 36 ml of methanol

Part U: 17.6 mg of the dyestuff of the formula



(FIAT report No. 943 of 25th April 1947), dissolved in 36 ml of methanol. The three emulsions S, T and U each contain 0.54 millimol of the dyestuff (4.5) bonded to gelatine. In addition the emulsions T and U contain, per mol of silver bromide, 0.035 and 0.14 millimol respectively of the dyestuff (4.6) adsorbed on the grain surface. Table 5 reproduces the sensitometric properties of the emulsions S, T and U.

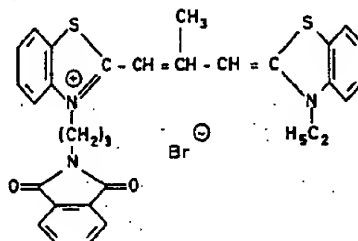
TABLE 5

1. Emulsion	Log E			5. Log E (-blue) -Log E (blue)	Sensitiser, mmol/mol of AgBr	
	2. white	3. blue	4. -blue		6. Bonded to gelatine	7. Adsorbed
S	-0.75	0.60	-0.68	-1.28	0.54	—
T	-0.84	0.58	-0.76	-1.34	0.54	0.035
U	-0.86	0.64	-0.80	-1.44	0.54	0.140

The dyestuff of the formula (4.5) can be manufactured as follows:

9.2 g of 2-methyl-3-(3-phthalimidopropyl)-benzthiazolium bromide and 7.3 g of 3-ethyl-2-(2-methylthio)-prop-1-enyl-benzthiazolium methyl sulphate in 250 ml of ethanol are boiled under a reflux condenser, until a clear solution is formed. After cooling to room temperature, 5 ml of trimethylamine are added to this solution. After further stirring for a quarter of an hour, the mixture is gradually warmed and then held for one hour at the boil under reflux. After cooling for two hours, the dyestuff is filtered off, washed with ethanol and ether and finally dried.

A solution of 2 g of the phthalimidopropyl dyestuff, thus obtained, of the formula

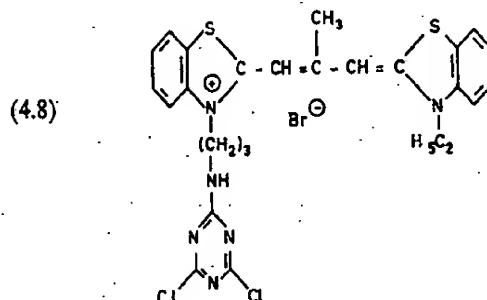


in 25 ml of 46% strength hydrobromic acid and 8 ml of water is boiled for 4 1/2 hours under a reflux condenser, whilst stirring. The clear red solution obtained on pouring out into water is treated with a solution of 18 g of sodium acetate in 100 ml of water, whilst stirring. The dyestuff which has precipitated is filtered off, washed with water and dried. It now contains a HBr.H₂N— group (aminopropyl dyestuff) in place of the phthalimide radical.

A mixture of 6.6 g of cyanuric chloride and 9.0 g of sodium bicarbonate in 350 ml of water is stirred at 33°C until virtually everything is in solution, which takes about 2 hours. After the small amount of insoluble residues has been filtered off, a solution of the aminopropyl dyestuff in 7 ml of water and 3 ml of 35.4% strength hydrochloric acid are added dropwise. After completion of the addition, the mixture is stirred for one hour at 30°C and a further 3.5 g of sodium bicarbonate in 50 ml of water are added and the red solution is stirred for a further hour at 30°C. The acetone is then distilled off under reduced pressure and at below 30°C, and the reaction mixture is left to stand overnight. The dyestuff of the formula (4.5) is filtered off, washed with three times 20 ml of water and dried in vacuo. λ_{\max} in methanol at 512 and 546 nm.

Example 5.

(a) A gelatine solution which contains the dyestuff of the formula

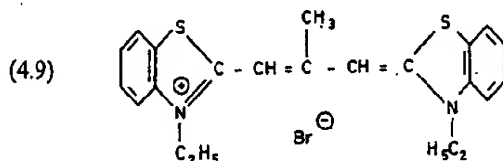


bound by covalent bonds to the gelatine is prepared as follows: 2 g of the sensitiser dyestuff (4.8) (3.14 mmol) are dissolved in 200 ml of N-methylformamide and the solution is added, at a temperature of 45°C, to 20 g of a 10% strength gelatine solution. The pH of the mixture is adjusted to 10 by adding 1 normal sodium hydroxide solution and the mixture is then stirred for a further 2 hours at 45°C. Thereafter the mixture is gradually cooled to -15°C and is flocculated, at a pH of 5.0, by means of acetone. The flocculate is taken up in water and the flocculation is repeated twice more. For further purification, the solution last obtained passes through a chromatography column with a dextran of bacterial origin modified by cross-linking of the linear macromolecules (SEPHADEX of Pharmacia Fine Chemicals AB, Uppsala Registered Trade Mark). An 0.5 molar sodium chloride solution adjusted to pH 3 by means of hydrochloric acid is used for elution. Finally, the eluate is dialysed until the chloride ions have disappeared completely and is then freeze-dried. The product obtained contains 0.11 mmols of the dyestuff (4.8) per g of dried gelatine. An analysis by means of gel chromatography no longer shows any detectable traces of free dyestuff.

A 4% strength aqueous solution which contains 4.4 mmol of the bound dyestuff (4.8) per litre is prepared from the gelatine preparation containing dyestuff. Thereafter the procedure of Example 8 is followed, by slowly dipping a silver bromide layer, which has been vapour-deposited on a carrier and been chemically sensitised, into this solution at 40°C, and lifting it out again.

The layer, which has now been optically sensitised, is now exposed behind a grey step wedge ($d = 0.3$) and two superposed orange filters which below a wavelength of 530 nm have a transmission of less than 0.1%, at a distance of 20 cm by means of an electronic flash for 1 millisecond. The latent image is developed in the same way as in Example 8 for minutes at room temperature and a silver image of the step wedge, with 8 visible steps, is obtained.

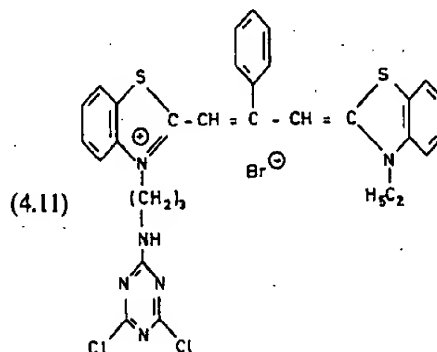
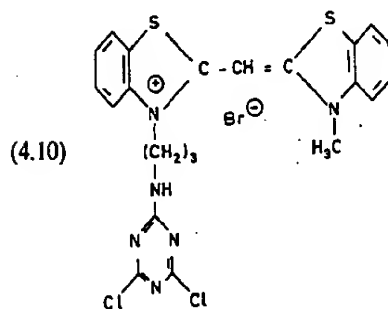
(b) The same result is achieved if in place of the dyestuff (4.8), which has been bound to gelatine as described above, the sensitiser dyestuff of the formula

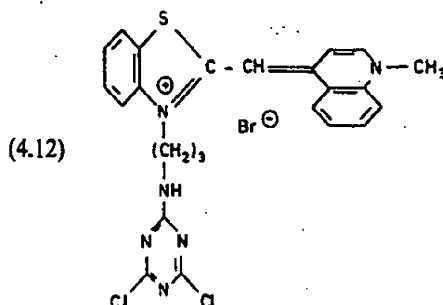


which has not been bound to gelatine is used in an aqueous solution containing 35% of methanol. In that case the sensitisation is carried out by customary adsorption, the vapour-deposited silver bromide layer being dipped for about 5 minutes into a solution containing 0.01 mmol per litre of the dyestuff (4.9).

(c) If the two treatments (a) and (b) described above are combined by treating the vapour-deposited layer first adsorptively with the aqueous methanolic solution of the dyestuff (4.9) and thereafter by brief dipping into the gelatine solution described above, containing the dyestuff (4.8) in bound form, a silver image is obtained, after exposure, in which 9 steps are visible, corresponding to a sensitivity increase by a factor of 2.

The same results as described above under (a), (b) and (c) are obtained if instead of the dyestuff (4.8) one of the dyestuffs of the formulae





is reacted with gelatine and used for sensitising the vapour-deposited layer according to (a) and the corresponding ethyl homologues which in place of the reactive dichlorotriazinyl group R contain an ethyl group are used for the treatment described under (b).

The reactive dyestuffs used in this example for the reaction with gelatine can be prepared as follows:

Reactive Dyestuff (4.8)

1.0 g of the amino-propyl dyestuff

(3-Ethyl-2-benzothiazole) (3-(3-aminopropyl)-2-benzothiazole) β -methyl trimethincyanine bromide hydrobromide, whose preparation was described in the foregoing example 4, was dissolved in 48% hydrobromic acid (2 ml) and water (4 ml) by warming on a steam bath. The clear solution was diluted with 2,2,2-trifluoroethanol (15 ml) and cooled to 0°C in an ice-bath. The stirred solution was cautiously neutralised with a solution prepared from anhydrous sodium carbonate (1 g) and water (5 ml) and the pink solution was treated with cyanuric chloride (2 g) at 0°C. The resulting mixture was stirred for 5 minutes and was treated with more sodium carbonate (0.8 g) in water (5 ml). Whilst maintaining this temperature more cyanuric chloride (0.5 g) was added and the mixture was stirred for an additional period of 10 minutes.

The deep violet solution containing some suspended matter, was stirred at 10°C for 1 hour (pH 7 to 8 on paper). After this period acetone (80 ml) was added to the solution which was poured into a solution of sodium hydrogen carbonate (2.5 g) in water (100 ml). Evaporation of the organic solvent under reduced pressure (bath temperature 30°C) afforded a gummy solid in the aqueous solution. The aqueous solution was diluted with water (100 ml) and refrigerated. The dark brown solid was filtered off and washed well with water (3 x 50 ml). The dye was triturated with acetone (40 ml) for a period of 10 minutes and the suspension was diluted with ether (150 ml). The dye was filtered off, washed with ether and dried.

Yield 0.95 g (85%) reactive dyestuff of formula (4.8).

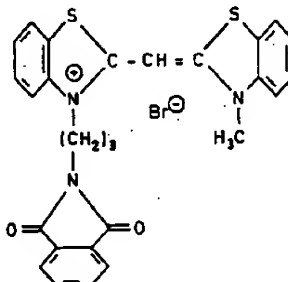
M.p. 292°C, sintered at 138°C.

λ_{\max} (acetonitrile) 543 nm.

Reactive Dyestuff (4.10)

A solution of 2-methyl-3-(3-phthalimidopropyl)benzothiazolium bromide (20.8 g, 0.05 M) in boiling ethanol (500 ml) was treated with a solution of 2-ethylmercapto-3-methyl benzothiazolium toluene-sulphonate (18.3 g, 0.05M). The resulting clear solution was cooled to room temperature. Triethylamine (20 ml) was added to the stirred solution over a period of 2 minutes and the dark solution was stirred at room temperature for a period of 10 minutes. A crystalline yellow solid deposited. The mixture was stirred and heated under reflux for a period of 1 hour. The dye was filtered from the boiling solution washed with methanol (3 x 75 ml) and dried.

Yield: 17 g dyestuff of formula



M.p. 275—278°C (decomp.)

λ_{\max} (methanol) 424 nm

The phthalimido dye (6.0 g) was treated with hydrobromic acid (48%, 93 ml) and water (18 ml) and the resulting mixture was stirred and heated under reflux until a clear solution was obtained. The clear solution was heated under reflux for an additional period of 2 hours. Upon cooling the solution to room temperature a yellow solid deposited. The mixture was triturated with acetone (450 ml) and the dye was filtered off, washed with acetone (2 x 50 ml) and dried under vacuum.

Yield 6.0 g of amino-propyl dyestuff

M.p. 309—310°C (decomp.)

λ_{max} (methanol) 422 nm

The foregoing aminopropyl dye (0.84 g) was treated with 48% hydrobromic acid (2 ml) and water (1 ml). The suspension was treated with 2,2,2-trifluoroethanol (30 ml) and the mixture was heated under reflux on a steam-bath until a clear solution was obtained. The warm solution (51°C) was stirred and cautiously neutralised with anhydrous sodium carbonate (1.2 g) in water (5 ml). After the addition of ca 4 ml of sodium carbonate solution, the resulting clear yellow solution was cooled to 5°C in an ice-bath. The turbid solution was treated with cyanuric chloride (2 g) and the remainder of the sodium carbonate solution.

The pale yellow turbid solution was stirred for 5 minutes at 0 to 5°C and was treated with more anhydrous sodium carbonate (0.3 g) in water (8 ml). The resulting mixture was stirred at 5°C for a period of 0.25 hours (pH 8.0) and was diluted with a mixture of acetone/water (1:1, 40 ml). The mixture was poured into a solution of sodium hydrogen carbonate (3 g) in water (40 ml). Evaporation of the organic solvent under reduced pressure (bath temperature 30°C) afforded a yellow solid in the aqueous phase. The dye was filtered off, washed with water (3 x 50 ml), triturated with acetone (25 ml) and the acetone solution was diluted with ether (150 ml). The solid was filtered off, washed with ether and dried.

Yield: 0.82 g of reactive dyestuff (4.10)

M.p. 279—284°C (decomp.)

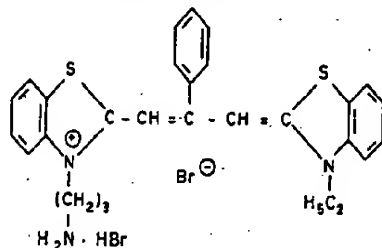
λ_{max} 423 nm (acetonitrile)

Reactive dyestuff (4.11)

A solution of 2-methyl-3-(3-phthalimidopropyl) benzothiazolium bromide (8.82 g) in boiling ethanol (225 ml) was cooled to 40°C and treated with 2-(β -chlorostyryl-3-ethyl) benzothiazolium chloride (12.2 g). The clear solution was treated with triethylamine (6 ml) and was gently heated under reflux for 1 hour. The solution on cooling at 0°C did not furnish a solid. Aqueous sodium bromide (10%, 150 ml) was added to the ethanolic solution which was evaporated under reduced pressure to eliminate the organic solvent. The aqueous solution deposited a tar which was separated by decantation. The tar was washed with water (500 ml). Attempts to crystallise the tar were unsuccessful.

Consequently, the tar was treated with 48% hydrobromic acid (170 ml) and water (60 ml) and the resulting mixture was stirred and heated under reflux for a period of 2 1/2 hours. The clear solution was poured into a solution of sodium acetate (prepared from 220 g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ and 800 ml water) and the solution was refrigerated overnight. The dye was filtered off, washed with water (50 ml), boiled in ethanol (100 ml) and the solution was diluted with ether (1 litre). The dye was filtered off, washed with ether (200 ml) and dried.

Yield: 13.7 g of the amino-propyl dyestuff of the formula



M.p. 187—192°C

λ_{max} 560 nm (methanol)

The foregoing aminopropyl dye (3.0 g) was dissolved in 48% hydrobromic acid (6 ml) at room temperature. The clear solution was diluted with water (3 ml) and

2,2,2-trifluoroethanol (40 ml). The resulting solution was cooled to 0°C in an ice bath. To the stirred solution aqueous sodium carbonate (12 ml), prepared from 3.9 g anhydrous sodium carbonate and water (15 ml) was added slowly. The vigorously stirred solution was treated with cyanuric chloride (3.7 g) and the remainder of the sodium carbonate solution (3 ml) at 0°C.

The resulting solution was stirred for 3 minutes and was treated with more sodium carbonate (1 g). Stirring was continued at 0°C for a period of 5 minutes after which time water (5 ml) was added. The dark violet solution was stirred for 10 minutes at 0°C treated with more water (20 ml) and the resulting solution was stirred for a further period of 10 minutes at 4°C. The solution was treated with acetone (75 ml) and was poured into a solution of sodium hydrogen carbonate (2 g) in water (50 ml) contained in a round bottom flask. Evaporation of the organic solvent under reduced pressure (bath temperature 30°C) afforded the dye in the aqueous solution. The dye was filtered off, washed with water (50 ml).

The dye was dissolved in boiling acetone (60 ml) and the solution was filtered. The filtrate was diluted with ether (500 ml). After cooling the solution to 10°C, the dye was filtered off, washed with ether and dried.

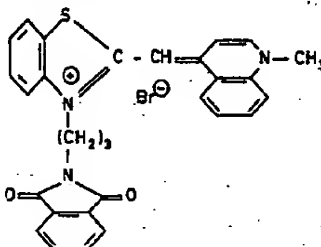
Yield: 1.4 g of the reactive dyestuff (4.11)

M.p. 219°C (decomp.), sintered at 163°C.

Reactive dyestuff (4.12)

A solution of 2-methyl-3-(3-phthalimidopropyl) benzothiazolium bromide (13.8 g) in boiling ethanol (345 ml) was stirred and treated with 1-methyl-4-methylthio quinolinium methylsulphate (10 g) and the clear solution was allowed to cool to 30°C. The mixture was treated with triethylamine (13 ml) and the temperature was gently raised to reflux. The dark orange solution was stirred and heated under reflux for 1 hour and the solution was refrigerated for 2 hours at 0°C. The orange dye was filtered off, washed well with ethanol, then with ether. The dye was dried at 50°C.

Yield: 14.3 g of the phthalimido dye of the formula



M.p. 281—282°C

λ_{max} 502 nm (methanol)

The foregoing phthalimido dye (14 g) was treated with 48% hydrobromic acid (170 ml) and water (60 ml) and the solution was stirred and heated under reflux for a period of 4 hours. The acidic solution was poured into a solution of sodium acetate (prepared from 220 g CH_3COONa , $3\text{H}_2\text{O}$ and water (1 litre). The dye precipitated on cooling the solution. The orange dye was filtered off, washed well with water, then acetone, and finally ether. The solid was dried under vacuum over KOH.

Yield: 12.3 g of phthalimido dye

M.p. 264—265°C (decomp)

λ_{max} 502 nm (methanol)

The aminopropyl dye (2.0 g) was dissolved in 48% hydrobromic acid (2 ml) and water (1 ml) by warming on a steam-bath. The clear solution was treated with 2,2,2-trifluoroethanol (40 ml) and the resulting solution was stirred and cooled to 0°C in an ice-bath. The solution was cautiously treated with aqueous sodium carbonate (4 ml, prepared from 1.3 g anhydrous sodium carbonate and 5 ml water) over a period of 5 minutes. Whilst maintaining this temperature cyanuric chloride (2.7 g) was added whereupon a gelatinous solid deposited. This was followed by the addition of the remainder of the sodium carbonate solution. The mixture was stirred and treated with more sodium carbonate (0.3 g) in water (3 ml). After the addition of the sodium carbonate solution, the mixture became less viscous and could be stirred more easily at 0°C. Water (5 ml) was added and the mixture was stirred at 4°C for a period of 10 minutes. More sodium carbonate (0.8 g)

in water (3 ml) was added to the mixture at 0°C to 4°C and the stirring was continued for an additional period of 5 minutes. A mixture of acetone/water (3:4, 70 ml) was added to the dye solution which was stirred at room temperature for a period of 5 minutes. Evaporation of the organic solvent under reduced pressure (bath temperature 30°C) afforded a dye in the aqueous solution. The dye was filtered from the aqueous solution (pH 4.0), triturated for 5 hours with 1% aqueous sodium hydrogen carbonate (200 ml), filtered and washed with water (3 x 50 ml).

Finally, the orange dye was triturated for 5 minutes with acetone (50 ml) and the mixture was diluted with ether (150 ml), stirred for a period of 10 minutes. The dye was filtered off, washed with ether (2 x 50 ml) and dried.

Yield: 2.1 g of reactive dyestuff (4.12)

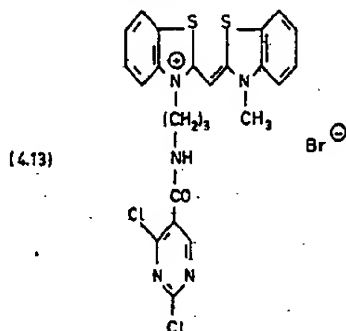
M.p. 190—194°C (decomp), sintered at 164°C

λ_{max} 501 nm (acetonitrile)

The following examples 12—16 concern the preparation of some more reactive dyes, which, according to the foregoing examples 1—5 may be reacted with a hydrophilic colloid, preferably gelatin and used to sensitise light-sensitive heavy metal compounds.

Example 6.

The reactive dyestuff of the formula



is prepared by reacting the aminopropyl dye used as a starting material for the preparation of compound (4.10) in example 11 with 2,4-dichloropyrimidine-5-carboxylic acid chloride in the following manner:

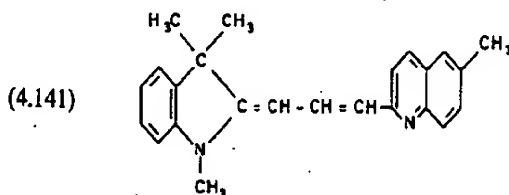
2.06 g of the aminopropyl dye were dissolved in 200 ml of water and 40 ml of acetone. The pH of the solution was adjusted to 4 by adding sodiumhydrogencarbonate solution. At 5°C 10.2 g of 2,4-dichloropyrimidine-5-carboxylic acid chloride in 30 ml acetone was added over 35 minutes keeping the pH at 4. The mixture was stirred for 20 minutes, the precipitate was filtered, washed with water, acetone and ether and dried in vacuo.

Yield: 0.8 g

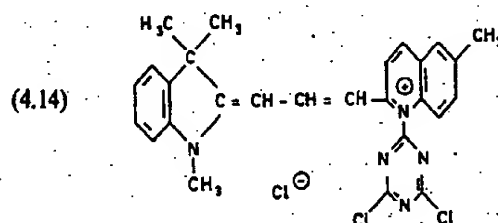
λ_{max} (methanol) = 425 nm

Example 7.

Starting from the compound



the reactive dye of formula



can be prepared in a single step by reacting it with cyanuric chloride in the following manner:

A solution of 2-[3-(6-methylen-2-quinolyl)-prop-2-enylidene]-1,3,3-trimethyl-indoline (0.50 g) in acetone (150 ml) was treated with a solution of cyanuric chloride (2.0) in acetone (200 ml). The resulting solution was stirred and heated under reflux for a period of 5 hours, and the pink solution was concentrated under reduced pressure to a low volume (10 ml). The solution was treated with ether (100 ml), left overnight at room temperature and the dye was filtered off, washed with acetone/ether (1:10, (200 ml) and dried.

Yield: 0.40 g

M.p. 234°C (decomp)

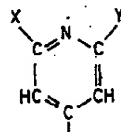
λ_{max} (acetone) 520 nm

The use of the spectral sensitizing dyes of this invention is described more fully in British Patent Application 11187/75 (Serial No. 1529201) from which this application was divided.

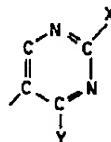
WHAT WE CLAIM IS:—

1. A spectral sensitising dinuclear cyanine dye or merocyanine dye which has attached either to a heterocyclic nucleus of the dye or to the methine chain of the dye an azine group which comprises at least one leaving group and which is reactive with a hydrophilic colloid which contains an SH—, NH₂—, NH=, OH—, —CONL₁L₂ group, where L₁ and L₂ are each hydrogen atoms or lower alkyl groups or a —COOH group.

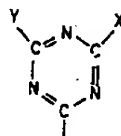
2. A spectral sensitising dinuclear cyanine dye or merocyanine dye according to claim 1, wherein the azine group is an azine radical of the general formula



or a diazine of the general formula

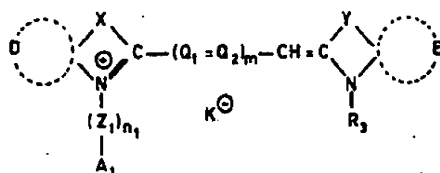


or a triazine of the general formula

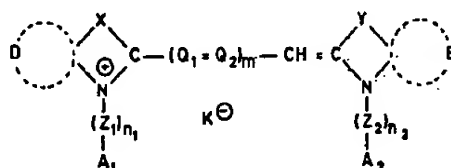


wherein in the above three formulae at least one of X or Y is a leaving group as hereinbefore defined and the other if not a leaving group is an hydroxy or lower alkoxy group.

3. A spectral sensitising dinuclear cyanine dye according to claim 1 of the general formula

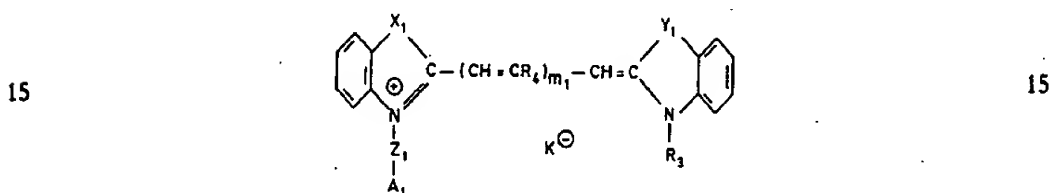


or the general formula



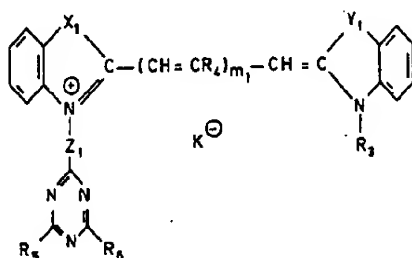
wherein the above two formulae X and Y are each $-\text{C}(\text{R}_1\text{R}_2)-$ where R_1 and R_2 are each hydrogen atoms or lower alkyl groups, $-\text{CH}=\text{CH}-$, $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$ or $-\text{NR}_7-$, where R_7 is a lower alkyl group, D and E each represent the atoms necessary to complete a benzene or naphthalene ring system which may be optionally substituted, m is 0, 1 or 2, Z_1 and Z_2 are each a linking group, each of n_1 and n_2 are 0 or 1, R_3 is a lower alkyl, lower alkoxy, carboxy lower alkyl or sulphy lower alkyl group, K is an anion, and A_1 and A_2 are azine groups which are reactive with a hydrophilic colloid which contains a reactable group as hereinbefore defined and $-(\text{Q}_1=\text{Q}_2)-$ represents a conjugated double bond system.

4. A spectral sensitising dinuclear cyanine dye according to claim 3 of the general formula



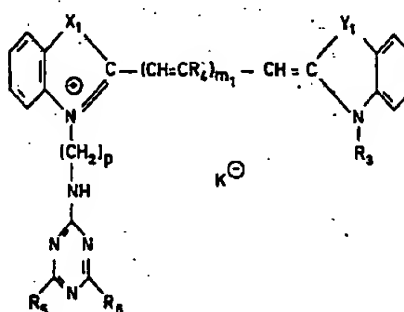
wherein X_1 and Y_1 are each $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$ or $-\text{NR}_7-$, R_4 is a hydrogen atom, a methyl, ethyl or phenyl group, and R_3 , R_7 , Z_1 , A_1 and K have the meanings assigned to them in claim 3 and m_1 is 0 or 1.

5. A spectral sensitising dinuclear cyanine dye according to claim 4 of the formula



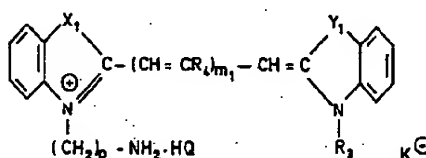
where at least one of R_5 and R_6 is a leaving group and the other if not such a group is an hydroxy or a lower alkoxy group, and X_1 , Y_1 , R_3 , R_4 , Z_1 , m_1 and K have the meanings assigned to them in claim 4.

6. A spectral sensitising dinuclear cyanine dye according to claim 5 of the formula

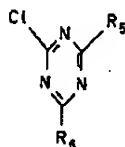


5 wherein X_1 , Y_1 , R_3 , R_4 , R_5 , R_6 , m_1 , p and K have the meanings assigned to them in claim 4.

7. A process for the preparation of a cyanine dye as claimed in claim 6 which comprises reacting a trimethincyanine dye of formula

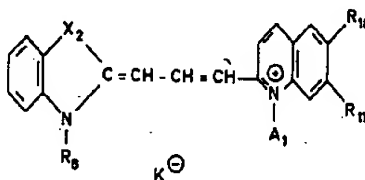


10 wherein X_1 , Y_1 , R_3 , R_4 , m_1 , p and K have the meanings assigned to them in claim 4 and Q is I , Cl or Br with a triazine of the general formula



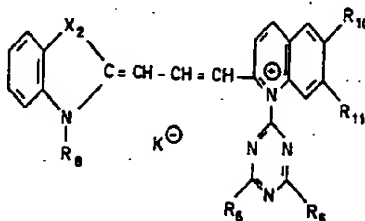
wherein R_5 and R_6 have the meanings assigned to them in claim 5.

8. A spectral sensitising dinuclear cyanine dye according to claim 3 of the general formula



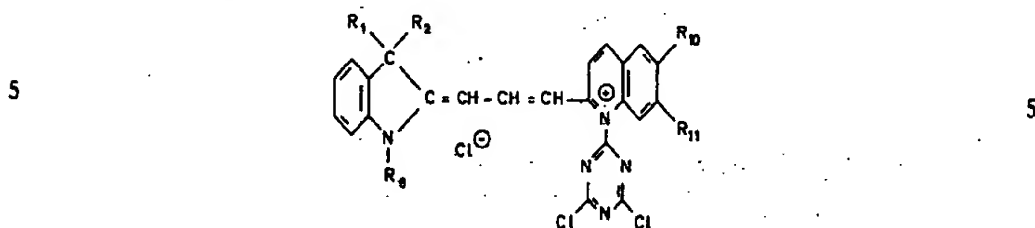
15 wherein X_2 is $-O-$, $-S-$, $-Se-$, $-NH-$ or $-C(R_1R_2)-$, R_{10} and R_{11} are each hydrogen atoms or lower alkyl or lower alkoxy groups, R_8 is lower alkyl, lower alkoxy, carboxy-lower alkyl or sulphy-lower alkyl and A_1 and K have the meanings assigned to them in claim 3.

20 9. A spectral sensitising dinuclear cyanine dye according to claim 8 of the general formula



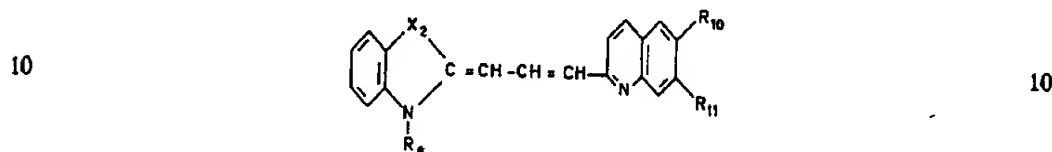
wherein X_2 , R_8 , R_{10} , R_{11} and K have the meanings assigned to them in claim 8 and R_3 and R_6 have the meanings assigned to them in claim 5.

10. A spectral sensitising dinuclear cyanine dye according to claim 9 of the general formula



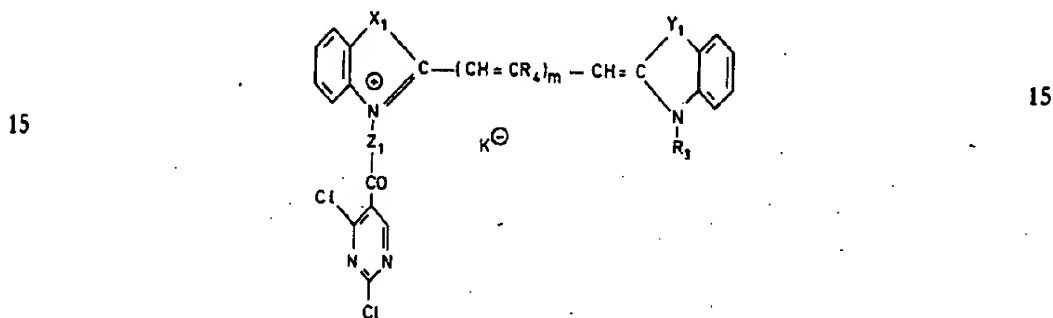
wherein R_1 , R_2 , have the meanings assigned to them in claim 3 and R_8 , R_{10} and R_{11} have the meanings assigned to them in claim 8.

11. A process for the production of the dinuclear cyanine dyes claimed in claim 9 which comprises reacting a cyanine base of the general formula



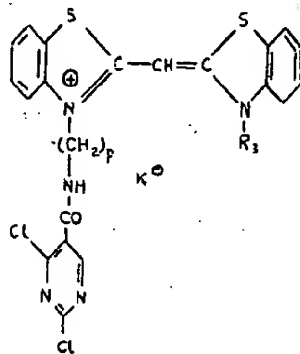
wherein X_2 , R_6 , R_{10} and R_{11} have the meanings assigned to them in claim 8 with a triazine of the general formula given in claim 7.

12. A spectral sensitising dinuclear cyanine dye according to claim 4 of the general formula

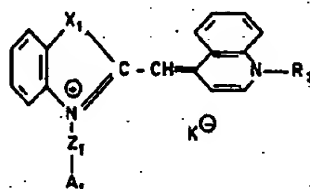


wherein X_1 , Y_1 , R_3 , R_4 , Z_1 , K and m have the meanings assigned to them in claim 4.

13. A spectral sensitising dinuclear cyanine dye according to claim 12 of the general formula

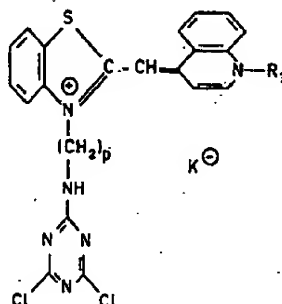


14. A spectral sensitising dinuclear cyanine dye according to claim 3 of the general formula



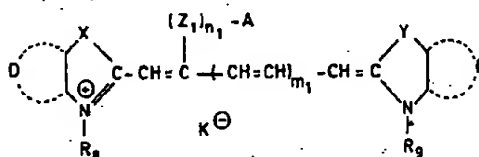
wherein A_1 , X_1 , R_3 , K and Z , have the meanings assigned to them in claim 4.

15. A spectral sensitising dinuclear cyanine dye according to claim 14 of the general formula



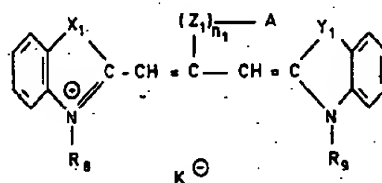
wherein R_3 and K have the meanings assigned to them in claim 14 and p is 2—5.

16. A spectral sensitising cyanine dye according to claim 1 of the general formula



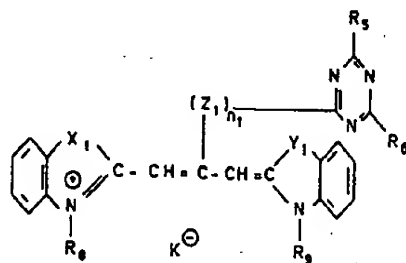
wherein X and Y are each $-C(R_1R_2)-$ wherein R_1 and R_2 are each a hydrogen or lower alkyl, $-CH=CH-$, $-O-$, $-S-$, $-Se-$ or $-NR_3-$, D and E each represent the atoms necessary to complete a benzene or naphthalene ring system which may be optionally substituted, m_1 is 0 or 1, R_1 and R_2 are each lower alkyl, lower alkoxy alkyl, carboxy lower alkyl or sulphy lower alkyl groups, Z_1 is a linking group, n_1 is 0 or 1, K is an anion, A is an azine group which is reactive with a hydrophilic colloid which contains a reactable group as hereinbefore defined.

17. A spectral sensitising cyanine dye according to claim 16 of the general formula



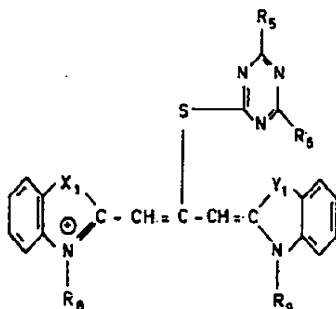
wherein X_1 and Y_1 are each $-O-$, $-S-$, $-Se-$ or $-NR_3-$ and K , Z_1 , n_1 , A , R_1 , R_2 and R_3 have the meanings assigned to them in claim 16.

18. A spectral sensitising cyanine dye according to claim 17 of the general formula



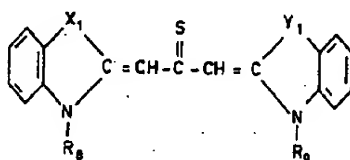
5 wherein X_1 , Y_1 , Z_1 , n_1 , R_8 , R_9 and K have the meanings assigned to them in claim 16 and R_5 and R_6 are leaving groups.

19. A spectral sensitising cyanine dye according to claim 18 of the general formula



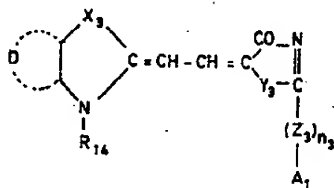
10 wherein X_1 , Y_1 , R_8 , R_9 , R_5 and K have the meanings assigned to them in claims 16 and 18.

20. A process for the production of a dye as claimed in claim 12 which comprises reacting a compound of the general formula



15 wherein X_1 , Y_1 , R_8 and R_9 have the meanings assigned to them in claim 16 with a triazine of the general formula defined in claim 7.

21. A spectral sensitising merocyanine dye of the general formula



20 wherein X_3 is $-C(R_1R_2)-$ wherein R_1 and R_2 are each a hydrogen atom or a lower alkyl group, $-CH=CH-$, $-O-$, $-S-$, $-Se-$ or $-NR_7-$ wherein Y_3 is $-O-$, $-S-$, $-Se-$ or $-NR_7-$, D represents the atoms necessary to complete a benzene or naphthalene ring system which is optionally substituted, R_{14} is lower alkyl, lower alkoxy, carboxy-lower alkyl or sulphony-lower alkyl, Z_3 is a linking group, n_3 is 0 or 1 and A_1 is an azine group which is reactive with a hydrophilic colloid which contains a reactable group as hereinbefore defined.

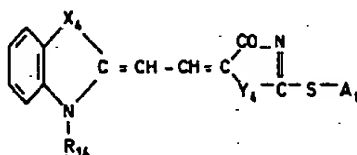
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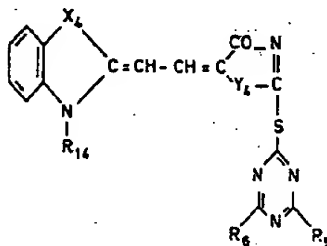
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22. A merocyanine dye according to claim 21 of the general formula



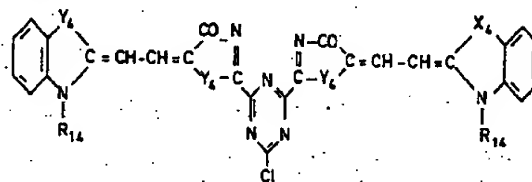
wherein X_4 is $-S-$, $-Se-$, $-NR-$ or $-O-$, Y_4 is $-O-$ or $-S-$ and R_{14} and A_1 have the meanings assigned to them in claim 21.

23. A merocyanine dye according to claim 22 of the general formula



wherein X_4 , Y_4 , R_5 , R_6 and R_{14} have the meanings assigned to them in claim 22.

24. A bis-merocyanine dye of the general formula



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wherein X_4 , Y_4 , and R_{14} have the meanings assigned to them in claim 23.

25. A spectral sensitising dinuclear cyanine dye according to claim 1 as prepared in any one of foregoing Examples.

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